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INTEGRATED PROCESS FOR THE CONVERSION OF FEEDSTOCKS CONTAINING COAL INTO LIQUID PRODUCTS

The present invention relates to an integrated process
10 for the conversion of feedstocks containing coal into liquid products.

It is known that the direct liquefaction of coal is based on hydrogenating treatment which leads to an increase in the hydrogen/carbon ratio from 0.7-0.8 to values higher
15 than a unit and typical of hydrocarbon mixtures of a petroleum origin.

This is a partial demolition, under hydrogenating conditions, of the organic structure of coal. Together with the liquid products, gases and solids are also formed in
20 quantities which vary in relation to the feedstock treated, the operating conditions and type of process.

Liquefaction is generally based on an essentially thermal reaction which causes the formation of radicals which are stabilized by hydrogen which has the function of
25 preventing their back-grading to give large less reactive

molecules, and on a catalytic hydrogenation which reduces the molecular complexity by splitting the bonds between various carbon atoms and other carbon atoms, oxygen, nitrogen and sulfur.

5 These two reactions can be carried out in a single step or in two separate steps.

 The result however is the breakage of the more complex hydrocarbon structures, accompanied by the reduction, or in appropriate cases, by the elimination of oxygen, nitrogen
10 and sulfur in the form of water, ammonia and hydrogen sulfide.

 The reactions are carried out in the presence of a solvent, normally produced in the process itself. The solvent has an essential role in the transformation, as it is
15 capable of extracting products rich in hydrogen and dissolving the complex molecules which are formed due to the effect of heat and is also capable of facilitating the reaction with hydrogen as transferor and donator. The ideal solvent must therefore have a high solvent capacity (and
20 therefore consist of a strongly aromatic structure by affinity with the type of solute) and good hydrogen donor characteristics (and must therefore be easy to hydrogenate and also easily release the hydrogen received to the coal).

 Products can be obtained from the liquefaction processes which vary from refined coal, still solid at room
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temperature, with a low content of sulfur and ashes, to light liquid products such as gasoline. In the former case, there are higher energy performances and weight yields; as the severity of the hydrogenation increases, when hydro-
5 cracking reactions become increasingly more significant, the quality of the liquid product improves but the yields decrease.

The approaches so far pursued for the liquefaction of coal to medium/light products can be synthetically and
10 schematically represented by the following process lines:

- high severity liquefaction in a single step;
- liquefaction with several steps having various degrees of severity.

In the former case, the thermal and catalytic reac-
15 tions take place in a single reactor, in a condition which is a compromise between the different optimum conditions for the two reactions: a severe hydrocracking is normally effected, obtaining products which can be distilled with great advantage in the delicate and onerous separation be-
20 tween liquids and non-reacted solids, which can take place by vacuum flash.

One of the disadvantages, however, is represented by a high production of gas, an undesired product, with a consequently considerable hydrogen consumption.

25 Using a multi-step scheme, it is possible to operate

under optimum conditions for the single reactors, thermal and catalytic (in particular the first liquefaction step can be carried out with a low severity, by effecting the transformation of coal in a liquid extract, with low gas
5 productions due to the low entity of hydrocracking reactions); but as most of the products cannot be distilled, it is necessary to resort to a more complex solid/liquid separation of vacuum distillation, such as treatment with an anti-solvent or filtration.

10 Finally, after the solid/liquid separation, the extract is subjected to a subsequent hydrocracking step under controlled catalytic conditions, to lighten the products.

The overall advantage derives from a better use of the hydrogen, with a lower overall consumption and a higher
15 process flexibility, resulting in a greater possibility of choice in the spectra of products.

Regardless of whether the liquefaction of coal is carried out in one or more steps, the coal liquids obtained must be heavily reprocessed with treatment units ad hoc
20 (hydrocracking effected with conventional technologies), as they are extremely aromatic, rich in nitrogen, sulfur and with a high density, to generate distillates having commercial characteristics.

It has now been found that by subjecting these liquids
25 obtained from the liquefaction of coal to certain further

conversion processes by means of hydrogenating treatment already used for the conversion of heavy crude oils or distillation residues, the conversion yields to DAO distillates can be maximized.

5 The hydrogenating processes for the conversion of heavy crude oils or distillation residues consist in treating the feedstock in the presence of hydrogen and suitable catalysts..

10 The hydroconversion technologies currently on the market use fixed bed or ebullated bed reactors and adopt catalysts consisting of one or more transition metals (Mo, W, Ni, Co, etc.) supported on silica/alumina (or an equivalent material).

15 Fixed bed technologies have considerable problems in treating particularly heavy feedstocks containing high percentages of hetero-atoms, metals and asphaltenes, as these contaminants cause a rapid deactivation of the catalyst.

20 Ebullated bed technologies were developed and commercialized for treating these feedstocks, which give interesting performances but are complex and costly.

25 Hydro-treatment technologies operating with catalysts in dispersed phase may constitute an attractive solution to the drawbacks which arise in the use of fixed bed or ebullated bed technologies. Slurry processes, in fact, combine the advantage of a wide flexibility with respect to the

feedstock with high performances in terms of conversion and upgrading, proving to be, at least in principle, simpler from a technological point of view.

Slurry technologies are characterized by the presence
5 of particles of catalyst having very small average dimensions and which are efficaciously dispersed in the medium; for this reason, hydrogenation processes are easier and more efficient in all points of the reactor. The formation coke is greatly reduced and the upgrading of the feedstock
10 is high.

The catalyst can be introduced as a powder with sufficiently reduced dimensions or as an oil-soluble precursor. In the latter case, the active form of the catalyst (generally the metal sulfide) is formed in situ by the thermal
15 decomposition of the compound used, during the reaction itself or after suitable pretreatment.

The metal constituents of the dispersed catalysts are generally one or more transition metals (preferably Mo, W, Ni, Co or Ru). Molybdenum and tungsten have much more satisfactory performances than nickel, cobalt or ruthenium and
20 even more so than vanadium and iron (N. Panariti et al., Appl. Catal. A: Gen. 2000, 204, 203).

Although the use of dispersed catalysts solves most of the problems listed for the technologies described above,
25 it also has disadvantages mainly linked to the life cycle

of the catalyst itself and the quality of the products obtained.

The conditions for the use of these catalysts (type of precursors, concentration, etc.) is in fact of great importance both from an economical point of view and also with respect to environmental impact.

The catalyst can be used at a low concentration (a few hundreds of ppm) in a "once-through" configuration, but in this case, the upgrading of the reaction products is generally insufficient (A. Delbianco et al., Chemtech, November 1995, 35). When operating with extremely active catalysts (for example molybdenum) and with higher concentrations of catalyst (thousands of ppm of metal), the quality of the product obtained becomes much better but the catalyst must be recycled.

The catalyst leaving the reactor can be recovered by separation from the product obtained from the hydro-treatment (preferably from the bottom of the distillation column downstream of the reactor) by the conventional methods such as decanting, centrifugation or filtration (US-3240718; US-4762812). Part of the catalyst can be recycled to the hydrogenation process without any further treatment. The catalyst recovered using the known hydro-treatment techniques, however, normally has a reduced activity with respect to the fresh catalyst so that a suitable regenera-

tion step is necessary in order to restore the catalytic activity and recycle at least part of said catalyst to the hydro-treatment reactor. Furthermore, said recovery procedures of the catalyst are costly and also extremely complex
5 from a technological point of view.

All the hydroconversion processes described above allow more or less high conversion levels to be reached depending on the feedstock and type of technology used, but generating a non-converted residue at the limit of stability, which we will call tar, which, from case to case, can
10 vary from 15 to 85% of the initial feedstock. This product is used for producing fuel oil, bitumens or it can be used as a feedstock in gasification processes.

In order to increase the overall conversion level of cracking processes of residues, schemes have been proposed
15 which envisage the recycling of more or less significant amounts of tar to the cracking unit. In the case of hydroconversion processes with dispersed catalysts in slurry phase, the recycling of the tar also allows the recovery of
20 the catalyst, to the extent that the same applicants have described, in patent application IT-95A001095, a process with allows the recycling of the recovered catalyst to the hydro-treatment reactor without the necessity of a further regeneration step, and at the same time obtaining a good-
25 quality product without the production of residue (zero

residue refinery).

This process comprises the following steps:

- mixing of the heavy crude oil or distillation residue with a suitable hydrogenation catalyst and sending of the mixture obtained to a hydro-treatment reactor introducing hydrogen or a mixture of hydrogen and H₂S therein;
- sending of the stream containing the hydro-treatment reaction product and the catalyst in dispersed phase to a distillation zone in which the most volatile fractions are separated (naphtha and gas oil);
- sending of the high-boiling fraction obtained in the distillation step to a deasphalting step, and consequent formation of two streams, one consisting of deasphalted oil (DAO), the other consisting of asphaltenes, catalyst in dispersed phase and possibly coke and enriched with the metals coming from the initial feedstock;
- recycling of at least 60%, preferably at least 80% of the stream consisting of asphaltenes, catalyst in dispersed phase and possibly coke, rich in metals, to the hydro-treatment zone.

It was subsequently found, as described in patent application IT-MI2001A-001438, that, in the case of the upgrading of heavy crude oils or bitumens from oil sands to complex hydrocarbon mixtures to be used as raw material for further conversion processes to distillates, it may be con-

venient to use different process configurations with respect to that described above.

The process described in patent application IT-MI2001A-001438 for the conversion of heavy feedstocks by the joint use of the following three process units: hydroconversion with catalysts in slurry phase (HT), distillation or flash (D), deasphalting (SDA), is characterized in that the three units operate on mixed streams consisting of fresh feedstock and recycled streams, using the following steps:

- sending of at least one fraction of the heavy feedstock to a deasphalting section (SDA) in the presence of solvents obtaining two streams, one consisting of deasphalted oil (DAO), the other of asphaltenes;
- mixing of the asphaltenes with the remaining fraction of heavy feedstock not sent to the deasphalting section and with a suitable hydrogenation catalyst and sending of the mixture obtained to a hydro-treatment reactor (HT) introducing hydrogen or a mixture of hydrogen and H_2S therein;
- sending of the stream containing the hydro-treatment reaction product and the catalyst in dispersed phase to one or more distillation or flash steps (D) whereby the most volatile fractions are separated, among which the gases produced in the hydro-treatment reaction, naphtha and gas oil;

- recycling of at least 60% by weight, preferably at least 80%, more preferably at least 95%, of the distillation residue (tar) or liquid leaving the flash unit, containing catalyst in dispersed phase, rich in metallic sulfides produced by the demetallation of the feedstock and possibly coke and various kinds of carbonaceous residues, to the deasphalting zone.

It is generally necessary to effect a flushing on the asphaltene stream leaving the deasphalting section (SDA) to ensure that all these elements do not accumulate too much in the hydro-treatment reactor and, in the case of the deactivation of the catalyst, to allow part of the catalyst to be removed, which is replaced with fresh catalyst. This however is generally not the case as the catalyst maintains its activity for a long period of time; considering that it is in any case necessary to effect a flushing for the reasons described above, some of the catalyst must obviously be used up even, it is far from being completely deactivated. Furthermore, although the volumes of flushing stream (0.5-4% with respect to the feedstock) are quite limited compared with other hydro-treatment technologies, there are still considerable problems relating to their use or disposal.

The application described is particularly suitable when the heavy fractions of complex hydrocarbon mixtures

produced from the process (at the bottom of the distillation column) must be used as feedstock for catalytic cracking plants, both Hydrocracking (HC) and Fluid Bed Catalytic Cracking (FCC).

5 The combined action of a catalytic hydrogenation unit (HT) with an extractive process (SDA) does in fact allow deasphalted oils to be produced with a reduced content of contaminants (metals, sulfur, nitrogen, carbonaceous residue), and which are therefore easier to treat in catalytic
10 cracking processes.

Another aspect to be considered, however, is that the naphtha and gas oil produced directly from the hydro-treatment unit still contain many contaminants (sulfur, nitrogen ...) and must in any case be reprocessed to obtain
15 end-products.

The integrated process, object of the present invention, for the conversion of feedstocks containing coal into liquid products by the joint use of at least the following seven process units: coal liquefaction (CL), flash or distillation of the product obtained from the liquefaction
20 (F), extraction with a solvent to remove the ashes (SDAsh), distillation to separate the solvent (RS), hydroconversion with catalysts in slurry phase (HT), distillation or flash of the product obtained from the hydroconversion (D),
25 deasphalting with a solvent (SDA),

is characterized in that it comprises the following steps:

- sending the feedstock containing coal to one or more direct coal liquefaction steps (CL) in the presence of a suitable hydrogenation catalyst;
- 5 • sending the stream containing the product obtained from the coal liquefaction reaction to one or more flash or distillation steps (F) obtaining a gaseous stream and a liquid stream;
- sending the liquid stream to an extraction step with a solvent (SDash) whereby an insoluble stream is obtained,
10 consisting of the mineral matter present in the feedstock and non-reacted coal and a liquid stream consisting of the liquefied coal obtained and the solvent used;
- sending the liquid stream consisting of the liquefied
15 coal and the solvent used to one or more distillation steps in order to substantially separate the solvent contained in the liquid stream, which is recycled to the extraction step with a solvent (SDash);
- mixing the liquid stream substantially consisting of the
20 liquefied coal and at least part of the stream containing asphaltenes obtained in the deasphalting unit with a suitable hydrogenation catalyst and sending the mixture obtained to a hydro-treatment reactor (HT) introducing hydrogen or a mixture of hydrogen and H₂S therein;
- 25 • sending the stream containing the reaction product of the

hydro-treatment and the catalyst in dispersed phase to one or more distillation or flash steps (D) whereby the different fractions coming from the hydro-treatment reaction are separated;

- 5 • sending at least part of the distillation residue (tar) or liquid leaving the flash unit, containing the catalyst in dispersed phase, rich in metal sulfides produced by the demetallation of the feedstock and optionally coke, to the deasphalting zone (SDA) in the presence of solvents, op-
- 10 tionally also fed by at least one fraction of the liquid stream substantially consisting of the liquefied coal, obtaining two streams, one consisting of deasphalted oil (DAO), the other containing asphaltenes.

The coal contained in the feedstock to be subjected to

15 the liquefaction step can be as such or optionally benefited by means of the known coal beneficiation treatment techniques.

The feedstock containing coal is preferably a feedstock substantially consisting of coal.

20 The suitable hydrogenation catalyst present in the liquefaction step (CL) can be at least partially recovered, recycled from the units downstream of said step (for example by means of the stream containing asphaltenes obtained in the deasphalting step (SDA) or by part of the distilla-

25 tion residue (tar) or liquid leaving the flash unit (D),

containing catalyst in dispersed phase, rich in metal sulfides produced by the demetallation of the feedstock and possibly coke.

The feedstock essentially consisting of coal is preferably slurried in a hydrocarbon matrix which can come from the units downstream of the liquefaction step (CL): preferably part of the stream containing asphaltenes, as well as the dispersed catalyst used in the hydro-treatment step (HT), obtained in the deasphalting step (SDA) and/or part of the stream consisting of deasphalted oil (DAO) obtained in the deasphalting step (SDA).

In the distillation step (RS) of the liquid stream consisting of liquefied coal and the solvent used, a further stream can be optionally separated, as distillate, which can be optionally added, either partly or totally, to the lighter fractions separated in the distillation or flash unit (D).

The direct liquefaction of the stream containing coal can be effected by adopting one of the various known coal liquefaction processes.

It may be advisable to effect the direct liquefaction of the stream containing coal by mixing said stream with an aromatic solvent, in a quantity ranging from 20 to 80% with respect to the coal, and with a suitable catalyst in dispersed phase, operating at a temperature ranging from 360

to 440°C, at a hydrogen pressure ranging from 3 to 30 MPa and with residence times less than or equal to 4 h.

The aromatic solvent used preferably comes, at least partially, from one or more of the following recycled
5 streams:

- part of the stream consisting of deasphalted oil (DAO) produced in the deasphalting step (SDA);
- at least part of the stream containing asphaltenes, as well as the dispersed catalyst used in the hydro-
10 treatment step (HT), produced in the deasphalting step (SDA);
- part of the medium and heavy fractions (medium and heavy distillates) obtained in the distillation or flash unit (D);
- 15 • part of the solvent separated in the distillation unit (RS) downstream of the ash removal step (SDAsh);
- part of the additional stream separated, as distillate in the distillation unit (RS) downstream of the ash removal step (SDAsh).

20 The extraction step with a solvent (SDAsh) to remove the ashes is preferably effected at a temperature ranging from 150 to 350°C and at a pressure ranging from 20 to 60 atm in the presence of a suitable aromatic solvent.

With respect to the general process, it is also possible to add a heavy feedstock, selected from heavy crude
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oils, distillation residues, heavy oils coming from catalytic treatment, thermal tars, bitumens from oil sands, various types of coals and/or other high-boiling feedstocks of a hydrocarbon origin known as black oils, to the feed-
5 stock consisting of coal to be sent to the liquefaction unit (CL) and/or to the liquid stream consisting of liquefied coal to be sent to the hydro-treatment step (HT).

A secondary post-treatment hydrogenating section of the C_2 -500°C fraction, preferably of the C_5 -350°C fraction,
10 deriving from the high pressure separating sections situated upstream of the distillation, can be present in addition to the steps forming the integrated process.

In this case, the stream containing the hydro-treatment reaction product and the catalyst in dispersed
15 phase, before being sent to one or more distillation or flash steps, is subjected to a separation pre-step effected at a high pressure in order to obtain a light fraction and a heavy fraction, said heavy fraction alone being sent to said distillation step(s) (D).

20 The light fraction obtained by means of the high pressure separation step can be sent to a hydro-treatment section producing a lighter fraction containing C_1 - C_4 gas and H_2S and a heavier fraction containing hydro-treated naphtha and gas oil.

25 The insertion of the secondary post-treatment hydro-

genating section of the C₂-500°C, preferably C₅-350°C, fraction exploits the availability of this fraction together with hydrogen at a relatively high pressure, which is approximately that of the hydro-treatment reactor, allowing the following advantages to be obtained:

- the production, starting from oil feedstocks extremely rich in sulfur, of fuels in line with the strictest specifications on the sulfur content (<10-50 ppm of sulfur) and improved with respect to other characteristics of diesel gas oil such as density, the content of polyaromatic hydrocarbons and the cetane number;
- the distillates produced do not suffer from problems of stability.

The hydrogenating post-treatment on a fixed bed consists in the preliminary separation of the reaction effluent of the hydro-treatment reactor (HT) using one or more separators operating at a high pressure and high temperature. Whereas the heavy part, extracted at the bottom, is sent to the main distillation unit, the part extracted at the head, a C₂-500°C, preferably C₅-350°C, fraction, is sent to a secondary treatment section in the presence of hydrogen, available at a high pressure, wherein the reactor is a fixed bed reactor and contains a typical desulfuration/dearomatization catalyst, in order to obtain a product having a much lower sulfur content and also lower levels of

nitrogen, a lower overall density and, at the same time, as far as the gas oil fraction is concerned, an increased cetane number.

5 The hydro-treatment section normally consists of one or more reactors in series; the product of this system can be further fractionated by distillation to obtain a totally desulfurated naphtha and a diesel gas oil according to specification as fuel.

10 The fixed bed hydro-desulfuration step generally uses typical fixed bed catalysts for the hydro-desulfuration of gas oils; said catalyst, or possibly also a mixture of catalysts or a series of reactors with several catalysts having different properties, causes a heavy refining of the light fraction, significantly reducing the sulfur and ni-
15 trogen content, increasing the hydrogenation degree of the feedstock, consequently reducing the density and increasing the cetane number of the gas oil fraction, at the same time reducing the formation of coke.

20 The catalyst generally consists of an amorphous part based on alumina, silica, silico-alumina and mixtures of different mineral oxides on which a hydro-desulfurating component combined with a hydrogenating agent, is deposited (with various methods). Catalysts based on molybdenum or tungsten, with the addition of nickel and/or cobalt depos-
25 ited on an amorphous mineral carrier are typical catalysts

for this type of operation.

The post-treatment hydrogenating reaction is carried out at an absolute pressure slightly lower than that of the primary hydro-treatment step, generally ranging from 7 to 14 MPa, preferably from 9 to 12 MPa; the hydro-desulfuration temperature ranges from 250 to 500°C, preferably from 280 to 420°C; the temperature is generally in relation to the desulfuration level required. The space velocity is another important variable in controlling the quality of the product obtained: it can range from 0.1 to 5 h⁻¹, preferably from 0.2 to 2 h⁻¹.

The quantity of hydrogen mixed with the feedstock is fed at a flow-rate ranging from 100 to 5000 Nm₃/m₃, preferably from 300 to 1000 Nm₃/m₃.

A further secondary post-treatment section of the flushing stream can be optionally present, alone or possibly together with the post-treatment hydrogenating section, in addition to the steps forming the integrated process.

Said further secondary post-treatment section consists in the post-treatment of the flushing stream in order to significantly reduce its entity and allow at least part of the catalyst, still active, to be recycled to the hydro-treatment reactor.

In this case, the fraction of stream containing asphaltenes, coming from the deasphalting section (SDA),

called flushing stream, is sent to a treatment section with a suitable solvent for the separation of the product into a solid fraction and a liquid fraction from which said solvent can be subsequently removed.

5 The possible treatment section of the flushing effluent, preferably in a quantity ranging from 0.5 to 10% by volume with respect to the fresh feedstock, consists of a de-oiling step with a solvent (toluene or gas oil or other streams rich in aromatic compounds) and a separation of the
10 solid fraction from the liquid fraction.

At least part of said liquid fraction can be fed:

- to the pool fuel oil, as such or after being separated from the solvent and/or after the addition of a suitable fluxing agent;
- 15 • and/or to the hydro-treatment reactor (HT) as such.

In specific cases, the solvent and fluxing agent can coincide.

The solid fraction can be disposed of as such or, more advantageously, it can be sent to a selective recovery
20 treatment of the transition metal or metals contained in the transition catalyst (for example molybdenum) (with respect to the other metals present in the starting residue, nickel and vanadium) with the optional recycling of the stream rich in transition metal (molybdenum) to the hydro-
25 treatment reactor (HT).

This composite treatment has the following advantages with respect to a traditional process:

- the entity of the flushing fraction is strongly reduced;
- most of the flushing fraction is upgraded to fuel oil by separating the metals and coke;
- the fraction of fresh catalyst to be added to the primary hydro-treatment feedstock is reduced as at least part of the molybdenum extracted from the selective recovery treatment is recycled.

10 The deoiling step consists in the treatment of the flushing stream, which represents a minimum fraction of the asphaltene stream coming from the deasphalting section (SDA) at the primary hydro-treatment plant of the heavy feedstock, with a solvent which is capable of bringing the
15 highest possible quantity of organic compounds to liquid phase, leaving the metallic sulfides, coke and more refractory carbonaceous residues (insoluble toluene or similar products), in solid phase.

20 Considering that the components of a metallic nature can become pyrophoric when they are very dry, it is advisable to operate in an inert atmosphere, containing as little oxygen and humidity as possible.

25 Various solvents can be advantageously used in this deoiling step; among these, aromatic solvents such as toluene and/or xylene blends, hydrocarbon feedstocks available

in the plant, such as the gas oil produced therein, or in refineries, such as Light Cycle Oil coming from the FCC unit or Thermal Gas oil coming from the Visbreaker/Thermal Cracker unit, can be mentioned.

5 Within certain limits, the operating rate is facilitated by increases in the temperature and the reaction time but an excessive increase is unadvisable for economic reasons.

10 The operating temperatures depend on the solvent used and on the pressure conditions adopted; temperatures ranging from 80 to 150°C, however, are recommended; the reaction times can vary from 0.1 to 12 h, preferably from 0.5 to 4 h.

15 The volumetric ratio solvent/flushing stream is also an important variable to be taken into consideration; it can vary from 1 to 10 (v/v), preferably from 1 to 5, more preferably from 1.5 to 3.5.

20 Once the mixing phase between the solvent and flushing stream has been completed, the effluent maintained under stirring is sent to a separation section of the liquid phase from the solid phase.

 This operation can be one of those typically used in industrial practice such as decanting, centrifugation or filtration.

25 The liquid phase can then be sent to a stripping and

recovery phase of the solvent, which is recycled to the first treatment step (de-oiling) of the flushing stream. The heavy fraction which remains, can be advantageously used in refineries as a stream practically free of metals and with a relatively low sulfur content. If the treatment operation is effected with a gas oil, for example, part of said gas oil can be left in the heavy product to bring it within the specification of pool fuel oil.

Alternatively, the liquid phase can be recycled to the hydrogenation reactor.

The solid part can be disposed of as such or it can be subjected to additional treatment to selectively recover the catalyst (molybdenum) to be recycled to the hydro-treatment reactor.

It has been found, in fact, that by adding a heavy feedstock but without metals such as, for example, part of the Deasphalted Oil (DAO) coming from the deasphalting unit of the plant itself, to the above solid phase, and mixing said system with acidulated water (typically with an inorganic acid), almost all of the molybdenum is maintained in the organic phase, whereas substantial quantities of other metals migrate towards the aqueous phase. The two phases can be easily separated and the organic phase can then be advantageously recycled to the hydro-treatment reactor.

The solid phase is dispersed in a sufficient quantity

of organic phase (for example deasphalted oil coming from the same process) to which acidulated water is added.

The ratio between aqueous phase and organic phase can vary from 0.3 to 3; the pH of the aqueous phase can vary
5 from 0.5 to 4, preferably from 1 to 3.

Various kinds of heavy feedstocks can be treated: they can be selected from heavy crude oils, bitumens from oil sands, various types of coals, distillation residues, heavy oils coming from catalytic treatment, for example heavy cy-
10 cle oils from catalytic cracking treatment, bottom products from hydroconversion treatment, thermal tars (coming for example from visbreaking or similar thermal processes), and any other high-boiling feedstock of a hydrocarbon origin generally known in the art as black oils.

15 As far as the general process conditions are concerned, reference should be made to what is already specified in patent applications IT-MI2001A-001438 and IT-95A001095.

According to what is described in patent application
20 IT-95A001095, all the heavy feedstock can be mixed with a suitable hydrogenation catalyst and sent to the hydro-treatment reactor (HT), whereas at least 60%, preferably at least 80% of the stream containing asphaltenes, which also contains catalyst in dispersed phase and possibly coke and
25 is enriched with metal coming from the initial feedstock,

can be recycled to the hydro-treatment zone.

According to what is described in patent application IT-MI2001A-001438, part of the heavy feedstock and at least most of the stream containing asphaltenes, which also contains catalyst in dispersed phase and possibly coke, are mixed with a suitable hydrogenation catalyst and sent to the hydro-treatment reactor, whereas the remaining part of the quantity of the heavy feedstock is sent to the deasphalting section.

According to what is described in patent application IT-MI2001A-001438, at least most of the stream containing asphaltenes, which essentially consists of said asphaltenes, is mixed with a suitable hydrogenation catalyst and sent to the hydro-treatment reactor, whereas all the heavy feedstock is fed to the deasphalting section.

When only part of the distillation residue (tar) or liquid leaving the flash unit is recycled to the deasphalting zone (SDA), at least part of the remaining quantity of said distillation or flash residue can be sent to the hydro-treatment reactor, optionally together with at least part of the stream containing asphaltenes coming from the deasphalting section (SDA).

The catalysts used can be selected from those obtained from precursors decomposable in-situ (metallic naphthenates, metallic derivatives of phosphonic acids, metal-

carbonyls, etc.) or from preformed compounds based on one or more transition metals such as Ni, Co, Ru, W and Mo: the latter is preferred due to its high catalytic activity.

The concentration of the catalyst, defined on the basis of the concentration of the metal or metals present in the hydroconversion reactor, ranges from 300 to 20,000 ppm, preferably from 1,000 to 10,000 ppm.

The hydro-treatment step is preferably carried out at a temperature ranging from 370 to 480°C, more preferably from 380 to 440°C, and at a pressure ranging from 3 to 30 MPa, more preferably from 10 to 20 MPa.

The hydrogen is fed to the reactor, which can operate with both the down-flow and, preferably, up-flow procedure. Said gas can be fed to different sections of the reactor.

The distillation step is preferably effected at reduced pressure ranging from 0.0001 to 0.5 MPa, preferably from 0.001 to 0.3 MPa.

The hydro-treatment step can consist of one or more reactors operating within the range of conditions specified above. Part of the distillates produced in the first reactor can be recycled to the subsequent reactors.

The deasphalting step, effected by means of an extraction with a solvent, hydrocarbon or non-hydrocarbon (for example with paraffins or iso-paraffins having from 3 to 6 carbon atoms), is generally carried out at temperatures

ranging from 40 to 200°C and at a pressure ranging from 0.1 to 7 MPa. It can also consist of one or more sections operating with the same solvent or with different solvents; the recovery of the solvent can be effected under
5 subcritical or supercritical conditions with one or more steps, thus allowing a further fractionation between deasphalted oil (DAO) and resins.

The stream consisting of deasphalted oil (DAO) can be used as such, as synthetic crude oil (syncrude), optionally
10 mixed with the distillates, or it can be used as feedstock for fluid bed Catalytic Cracking or Hydrocracking treatment.

Depending on the characteristics of the crude oil (metal content, sulfur and nitrogen content, carbonaceous
15 residue), the feeding to the whole process can be advantageously varied by sending the heavy residue alternately either to the deasphalting unit or to the hydro-treatment unit, or contemporaneously to the two units, modulating:

- the ratio between the heavy residue to be sent to the hydro-treatment section (fresh feedstock) and that to be
20 sent for deasphalting; said ratio preferably varies from 0.01 to 100, more preferably from 0.1 to 10, even more preferably from 1 to 5;
- the recycling ratio between fresh feedstock and tar to be
25 sent to the deasphalting section; said ratio preferably

varies from 0.01 to 100, more preferably from 0.1 to 10;

- the recycling ratio between fresh feedstock and asphaltenes to be sent to the hydro-treatment section; said ratio can vary in relation to the variations in the previous ratios;

- the recycling ratio between tar and asphaltenes to be sent to the hydro-treatment section; said ratio can vary in relation to the variations in the previous ratios.

This flexibility is particularly useful for fully exploiting the complementary characteristics of the deasphalting units (discrete nitrogen reduction, and de-aromatization) and hydrogenation units (high removal of metals and sulfur).

Depending on the type of crude oil, the stability of the streams in question and quality of the product to be obtained (also in relation to the particular treatment downstream), the fractions of fresh feedstock to be fed to the deasphalting section and hydro-treatment section can be modulated in the best possible way.

The application described is particularly suitable when the heavy fractions of the complex hydrocarbon mixtures produced by the process (bottom of the distillation column) are to be used as feedstock for catalytic cracking plants, both Hydrocracking (HC) and fluid bed Catalytic Cracking (FCC).

The combined action of a catalytic hydrogenation unit (HT) with an extractive process (SDA) allows deasphalted oils to be produced with a reduced content of contaminants (metals, sulfur, nitrogen, carbonaceous residue), and which
5 can therefore be more easily treated in the catalytic cracking processes.

A preferred embodiment of the present invention is provided hereunder with the help of the enclosed figure 1 which, however, should in no way be considered as limiting
10 the scope of the invention itself.

A feedstock (1) substantially consisting of coal, after being preferably slurrified in a hydrocarbon matrix, a suitable solvent (2) and an appropriate hydrogenation catalyst (3) are sent to the direct liquefaction unit (CL),
15 into which hydrogen or hydrogen and H_2S (4) are introduced and from which a stream (5) leaves, which is subjected to a flash step (F) in order to obtain a gaseous stream (6) and a carbonaceous liquid stream (7).

The carbonaceous liquid stream (7) is fed to the extraction unit with a solvent (SDA) whereby an insoluble
20 stream (8) is obtained, consisting of the mineral matter present in the feedstock and non-reacted coal and a liquid stream (9) consisting of the liquefied coal obtained and the solvent used, the latter stream (9) being sent in turn
25 to a distillation step (RS) in order to separate the sol-

vent (10) contained therein, to be recycled to the extraction unit (SDAsh), from a further liquid stream (11).

An additional stream (12) can be optionally separated, as distillate, and possibly added (13) to the lighter fractions separated in the distillation or flash unit (D) and/or recycled (14), as solvent, to the liquefaction unit (CL).

The liquid stream (11) consisting of liquefied coal mixed with a suitable hydrogenation catalyst (15), is fed to a hydro-treatment unit (HT) introducing hydrogen or hydrogen and H_2S (16) therein, from which a stream (17) is obtained, containing the hydrogenation product and the catalyst in dispersed phase, which is fractionated in a distillation column (D), from which the lighter fractions are separated (18) together with the distillable products (19), (20) and (21) from the distillation residue (22) containing the dispersed catalyst and coke.

Said distillation residue (22), called tar, is sent to the deasphalting unit (SDA) so as to obtain two streams: one (23) consisting of deasphalted oil (DAO), the other (24) consisting of asphaltenes which can be partly or totally added (25) to the liquid stream (11) consisting of liquefied coal and optionally partially recycled (26) to the feedstock substantially consisting of coal (1).

Some examples are provided hereunder for a better il-

lustration of the invention, but should in no way be considered as limiting the scope of the invention itself.

EXAMPLE 1

The following experiment was effected, following the scheme represented in Figure 1.

Liquefaction step

- Reactor: 30 cc made of steel equipped with a capillary stirring system and the possibility of reintegrating the hydrogen.
- Feedstock: 5.0 g of Columbian coal El Cerrejon (Table 1)
- Solvent: 5.0 g of hydro-treated DAO
- Catalyst: 200 ppm of Mo(introduced as hydro-soluble precursor)
- Temperature: 400°C
- Residence time: 2 h
- Pressure: 15 MPa

The coal liquefaction step was carried out according to the operating conditions indicated above. When the test had been completed, the quenching of the reaction was effected; the autoclave was depressurized and the gases collected in a sampling bag for gas chromatographic analysis. The non-gaseous products present in the reactor were recovered with THF and filtered on 0.5 μ m Teflon filters to eliminate the THF-insoluble components consisting of the inorganic material (ashes), the non-reacted organic frac-

tion and the catalyst.

The conversion was calculated according to the following equation:

$$\text{Conversion} = (\text{coal}_{\text{maf}} - \text{IOM}) / (\text{coal}_{\text{maf}}) * 100$$

- 5 In the formula specified above, the weight of coal is given on the basis of maf (moisture and ash free), i.e. the total weight of coal was subtracted from the ash and water part. IOM (insoluble organic matter) refers to the part of THF-insoluble products recovered at the end of the reaction
- 10 from which the ash and water part was subtracted.

Hydro-treatment step of liquids from coal:

- Reactor: 30 cc made of steel equipped with a capillary stirring system and the possibility of reintegrating the hydrogen.
- 15 • Feedstock: 10 g of liquids from coal produced from the liquefaction step
- Catalyst: 3000 ppm of Mo (introduced as hydro-soluble precursor)
- Temperature: 415°C
- 20 • Residence time: 4 h
- Pressure: 16 MPa

When the test had been completed, the quenching of the reaction was effected; the autoclave was depressurized and the gases collected in a sampling bag for gas chromatographic analysis. The non-gaseous products present in the

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reactor were recovered with THF and filtered on 0.5 μm Teflon filters to separate the THF-insoluble components consisting of the catalyst, metal sulfides and possible traces of coke produced. The THF-soluble fraction was then treated with an excess of n-pentane to precipitate the C_5 asphaltenes and produce a DAO (Deasphalted Oil) to be analyzed by means of GC SIM-DIST for the determination of the distillates, or quantifying the yields to:

- naphtha (PI-170°C)
- atmospheric gas oil (170-350°C)
- vacuum gas oil (350-500°C)
- vacuum residue (500°C+)

Experimental results

The data relating to the liquefaction step and subsequent hydrogenating treatment are indicated in Table 2.

Table 1: coal characterization

COAL	Humidity (w%)	Volatiles (w%)	Ash (w%)	C (w%)	H (w%)	N (w%)	S (w%)
El Cerrejon Colombia	5.25	35.46	4.71	73.7	5.35	1.41	0.61

Table 2: results of the liquefaction and hydro-treatment test

TEST	Conv, (w%)	THFI (w%)	ASFC ₅ (w%)	C ₁ -C ₄ (w%)	C ₅ - 170°C (w%)	170- 350°C (w%)	350- 500°C (w%)	500°C+ (w%)
Liquefaction step	81	8.7	37.9	1.4	--	--	--	--
Hydro- treatment step	--	1.0	4.1	2.6	0.2	10.2	27.0	40.5

EXAMPLE 2

The same procedure is adopted as described in Example 1; 5.0 g of coal are treated together with 5.0 g of DAO solvent, in the presence of a solid mixture containing molybdenum sulfide, metal sulfides and heavy carbonaceous material. The above mixture derives from hydro-treatment tests of heavy hydrocarbon feedstocks and represents part of the bottom of the deasphalting column ("flushing" stream of Figure 1). A quantity of solid mixture is introduced into the reactor, which is such as to obtain a concentration of molybdenum equal to 200 ppm.

Table 3 indicates the data relating to the coal liquefaction test.

Table 3: results of the liquefaction test

TEST	Conv, (w%)	THFI (w%)	ASFC ₅ (w%)	C ₁ -C ₄ (w%)
Liquefaction step	79	10.6	38.2	1.5

EXAMPLE 3

Following the scheme represented in Figure 1, the following experiment was effected.

10 Liquefaction step

- Reactor: 3000 cc made of steel equipped with a magnetic stirring system and the possibility of reintegrating the hydrogen.
- Feedstock: 250 g of coal (Table 1)
- 15 • Solvent: 250 g of LCO (Light Cycle Oil)
- Catalyst: 500 ppm of Mo(introduced as hydro-soluble precursor)
- Temperature: 415°C
- Residence time: 4 h
- 20 • Pressure: 16 MPa

When the test had been completed, the quenching of the reaction was effected; the autoclave was depressurized and the gases collected in a sampling bag for gas chromatographic analysis.

25 The product was recovered from the reactor and sub-

jected to filtration to separate the THF-insoluble components consisting of the inorganic material (ashes), from the non-reacted organic fraction and the catalyst.

5 The liquefaction step was repeated several times in order to obtain a quantity of liquid sufficient for the subsequent hydro-treatment tests.

Reference is made to the data indicated in Tables 2 and 3 for the results in terms of coal conversion.

Flash step

10 The light fraction (350°C-) consisting of the solvent used in the liquefaction step and the distillates produced by the reaction, were separated by means of batch distillation.

Hydro-treatment step

15 The hydro-treatment reaction was effected under the conditions specified in Example 1, using the product obtained from the flash step (column bottom, 350°C+ residue).

The gaseous products were separated at the end of the hydrogenation step. The product was then deasphalted by
20 means of liquid propane. The C₃ DAO produced was then separated and recovered. 8 consecutive hydro-treatment tests were effected, using for each test a feedstock consisting of 350°C+ residue obtained from the coal liquefaction and C₃ asphaltenes obtained from the previous hydro-treatment
25 step and subsequent deasphalting, containing the catalyst,

so as to allow the complete recycling of the catalyst added during the first test. At each step, a quantity of residue from coal liquids was added, so as to continuously operate on the same quantity of total feedstock (approx. 300 g).

5 The ratio between the quantity of coal liquids and quantity of recycled product reached under these operating conditions was 1:1.

10 The data relating to the outgoing streams after the last recycling (weight % with respect to the liquid feedstock introduced) are provided hereunder:

- Gas: 7%
- Naphtha (C₅-170°C): 8%
- Atmospheric gas oil (AGO 170-350°C): 19%
- Deasphalted oil (VGO + DAO): 66%

15 In the example indicated it was not necessary to effect a flushing of the recycled stream.

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